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# SELECTIVE SEPARATION OF CADMIUM FROM ZINC AND COPPER(II) WITH CRYSTALLINE ANTIMONIC(V) ACID AS A CATION-EXCHANGER*

Mitsuo ABE
Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

Crystalline antimonic(V) acid (C-SbA) shows an extremely high value of distribution coefficient for Cd(II), and the low values for Zn(II) and Cu(II) in nitric acid media. The Zn(II) and Cu(II) can be separated selectively from Cd(II) with the C-SbA using a 3M nitric acid as an eluant.

Ion-exchange separations of cadmium ion from other elements have received considerable attention during last two decades. Especially the separation factor for zinc-cadmium pair is very small on cation-exchange resins of strong acid type. Most methods are based on the separation of the metal ions as halide complex. Cation-exchange methods were applied first to the separation of cadmium ions from zinc ions in dilute hydrochloric acid as an eluant.[1,2] The separation factors are increased by the addition of an appreciable amount of water-miscible organic solvents such as alcohols, acetone etc.[3,4] Yet the separation factors between zinc and cadmium are not very large.

The stability of cadmium-halide complex increases quite distinctly in order; chloride < bromide < iodide.[5] Anion-exchange methods were also applied to the separation of cadmium from other elements. The use of hydrobromic acid or hydroiodic acid solution provides a very selective separation method of cadmium ions from zinc ions by anion-exchange resins, but it was not very successful because of some tailing of zinc ions.[6-8]

Analytical applications of inorganic ion-exchange materials have also received considerable attention owing to their high selectivities with respect to certain elements.[9,10] Among these inorganic cation-exchanger, the C-SbA shows high selectivities for various metal ions and can be applied to the effective separation for alkali metals and alkaline earth metal ions by using a relatively small column.[11-14] This paper describes a procedure for the selective separation of cadmium(II) from zinc(II) and copper(II) ions with the C-SbA by means of chromatographic technique.

The C-SbA was prepared as described previously.[15] The distribution coefficients (Kd) of the metal ions were determined by shaking 0.25g of the C-SbA with 25.0 ml of a solution containing $1 \times 10^{-4}$mol/l of a transition metal ion. After equilibration the metal ions were analyzed by atomic absorption spectrometry. The Kd values were calculated from

$$Kd = \frac{\text{amount of the metal ions in exchanger}}{\text{amount of the metal ions in solution}} \times \frac{\text{ml of solution}}{\text{g of exchanger}}$$

The Kd values obtained in various solutions are summarized in Table 1.

Table 1. The Kd values of Cd(II), Zn(II) and Cu(II) on the C-SbA at 30°C

| Solution | Cd(II) | Zn(II) | Cu(II) |
|---|---|---|---|
| 0.7M $HNO_3$ | >$10^4$ | 2.5 | 8.1 |
| 2M HCl | 310 | 4.9 | 15.7 |
| 2M HCl (80% ethanol) | 2.1 | <1.5 | 66.6 |

The Kd value of cadmium ions is extremely high in the nitric acid solution, while very low for zinc ions and copper(II) ions, so that the zinc and copper(II) ions should be eluted with a small volume of the nitric acid solution at relatively high concentration and the cadmium ions may be retained on the C-SbA column.

A small column containing 0.3 g of the C-SbA (100-200 mesh size) was prepared with 2.0 x 0.4 cm i.d., and was pretreated with 10 ml of a 3M nitric acid solution. A sample solution (2.0 ml) containing 1 x $10^{-3}$mol/l of these metal ions in 3M nitric acid was then added onto the C-SbA column. An eluant of 3M nitric acid was injected continuously on the C-SbA column. The sharp elutions of zinc and copper (II) ions were observed with less tailing effect and the cadmium ions were retained on the column even by a concentrated nitric acid solution (Fig.1).

The data of the Kd values in Table 1 indicates that the elution of cadmium ions may be possible by using the hydrochloric acid at a relatively high concentration. The elution curve of cadmium ions was observed with long tailing even by using a 2M hydrochloric acid solution of 80% ethanol.

It has been known that acetone is the most effective of solvents to promote metal-complex formation for selective elution of the metal ions from cation-exchange resins.[3)] More effective elution of cadmium ions was observed by using a solution of 1M hydrochloric acid- 50% acetone than that of a solution of 2M hydrochloric acid-80% ethanol, but long tailing was still observed (Fig.1).

The heated column was then applied to perform more rapid elution. The heated column consisted of a pyrex tube (2.0 x 0.4 cm i.d.) filled with 0.3 g of the C-SbA and of an outside jacket through which thermostatic water at 50°C is pumped. Better elution was performed than the other eluants, but some tailing was still observed.

It has been reported that the lattice constant of the C-SbA in hydrogen ion form decreased from 1.038 nm to 1.026 nm by the ion-exchange of cadmium, while increased to 1.048 nm by the ion-exchange of potassium without change in the space group (Fd3m) of the crystal system.[16,17)] An eluant containing 0.5M potassium chloride in 1M hydrochloric acid-50% acetone solution has been tested in order to improve the elution of cadmium, because the expansion of the lattice of the C-SbA seems to be useful for the rapid elution of the element. The proposed eluant for cadmium completely eliminates the tailing observed on the other eluants (Fig.1).

A rapid and quantitative separation of cadmium from zinc and copper (II) was performed with much less tailing effect by using the heated C-SbA column at 50°C. The cadmium in the last 80 ml of the eluate remained below the detection limit of

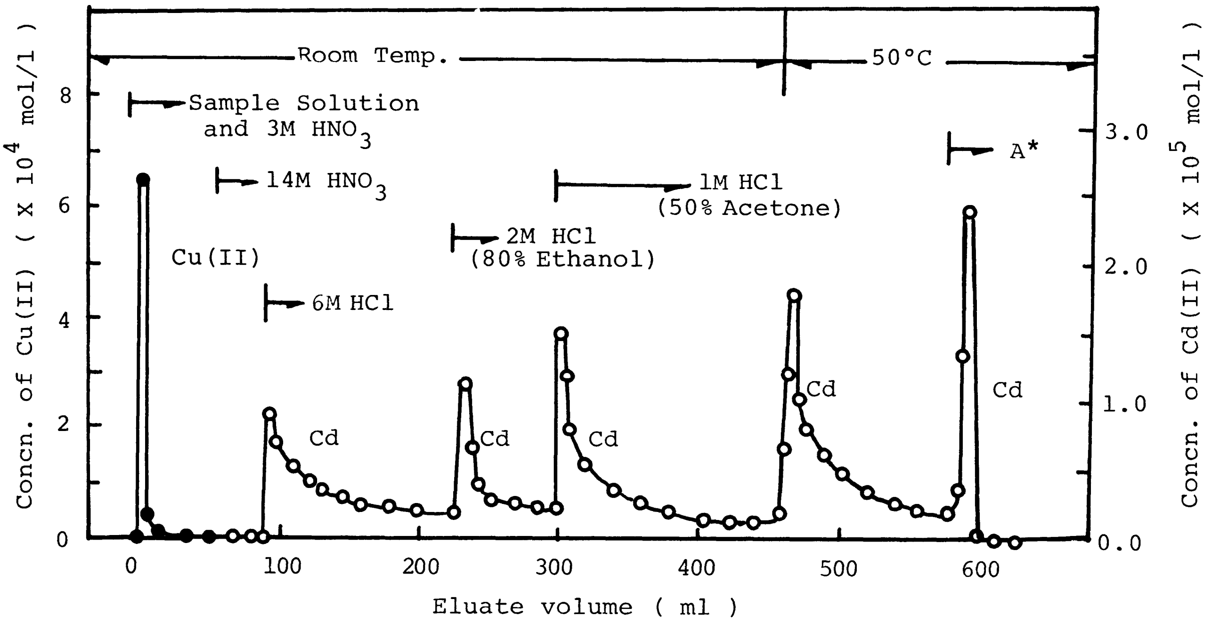


Fig.1. Elution curves of Cu(II) and Cd(II) at various eluants
Column, 2.0 X 0.4 cm i.d.; flow rate, 1.0 ± 0.5 ml/min
A* eluant, 0.5M KCl + 1M HCl in 50% Acetone solution

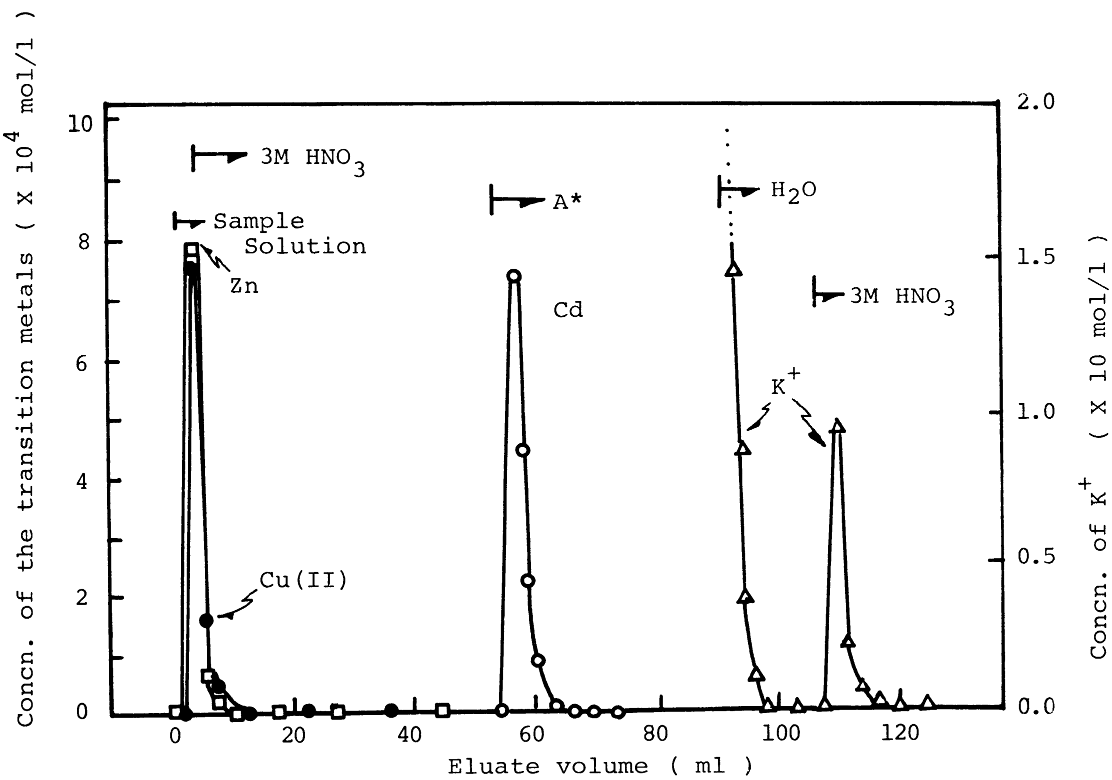


Fig.2. Elution curves for Zn(II), Cu(II), Cd(II) and $K^+$ with the C-SbA column heated at 50°C

Column, 2.0 X 0.4 cm i.d.; flow rate, 1.0 ± 0.5 ml/min
A* eluant, 0.5M KCl + 1M HCl in 50% acetone solution

the atomic absorption method (0.01 ppm) (Fig.2).

The potassium ions adsorbed by injection of the solution of 0.5M potassium chloride-1M hydrochloric acid-50% acetone was eluted easily by using a 3M nitric acid solution as an eluant.

The C-SbA column can therefore be used repeatedly as a usual column operation condition.

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